Sugar-Based Photoacid Generators ("Sweet" PAGs): Environmentally Friendly Materials for Next Generation Photolithography

(*Task Number: 425.029*)

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PIs:

- **Christopher K. Ober, Materials Science and Engineering, Cornell University**
- **Reyes Sierra, Chemical and Environmental Engineering, UA**

Graduate Students:

- **Lila Otero, PhD candidate, Chemical & Environmental Engineering, UA**
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Undergraduate Students:

- **Lily Milner, Chemical & Environmental Engineering, UA**

Other Researchers:

- **Youngjin Cho, Postdoctoral Fellow, Materials Science & Eng., Cornell University**
- **Wenjie Sun, Postdoctoral Fellow, Chemical & Environmental Engineering, UA**

Cost Share (other than core ERC funding):

- **UofA GIGA fellowship (1 year) to Lila Otero.**

Objectives

- **Develop PFOS-free and environmentally friendly PAGs with superior imaging performance. The novel PAGs will be based on biological units such as sugars and cholic acids for chemically amplified resist application**

- **Identify modeling tools to predict the environmental fate of novel PAGs**

- **Evaluate the environmental aspects of new PAGs**

ESH Metrics and Impact

1. **Reduction in the use or replacement of ESH-problematic materials**

   Complete replacement of perfluorooctanesulfonate (PFOS) structures including metal salts and photoacid generators in photoresist formulations.

2. **Reduction in emission of ESH-problematic material to environment**

   Develop new PAGs that can be readily disposed of in ESH friendly manner.

3. **Reduction in the use of natural resources (water and energy)**

   New PAGs prepared using simple, energy reduced chemistry in high yields and purity to reduce water use and the use of organic solvents.

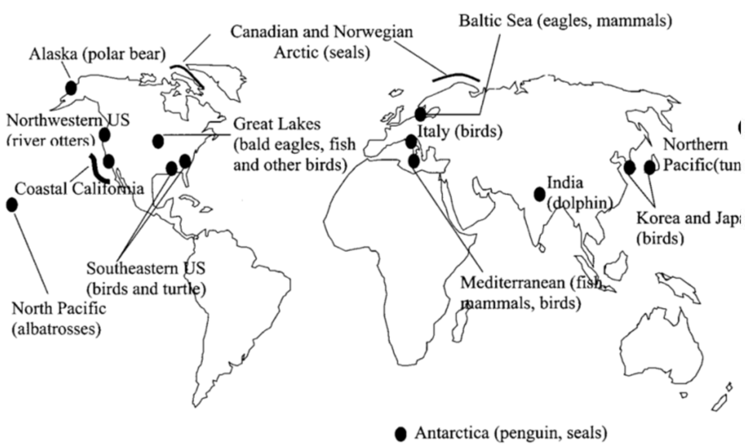
4. **Reduction in the use of chemicals**

   Reduction in the use of fluorinated chemicals.

PFOS is a Persistent, Toxic and Bioaccumulative (PBT) Contaminant

❯ **PFOS and PFOS-related materials are potentially environmentally hazardous**

Global Distribution of PFOS in Wildlife



Environ. Sci. Technol. 2001, *35*, 1339.

PFOS in human blood

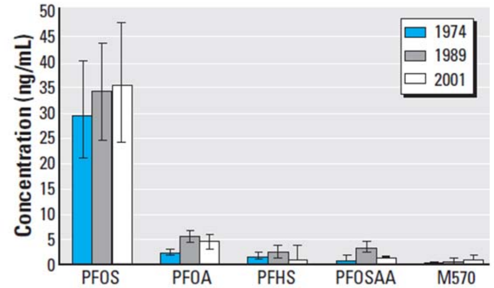


Figure 1. Median fluorochemical concentrations and IQRs for blood samples collected in Washington County, Maryland, from adults living in proximity in 1974 (*n* = 178 serum samples) and 1989 (*n* = 178 plasma samples) and in the county in 2001 (*n* = 108 serum samples; Olsen et al. 2003c).

Environ. Health Perspect. 2005, *113*, 539.

PFOS in drinking water

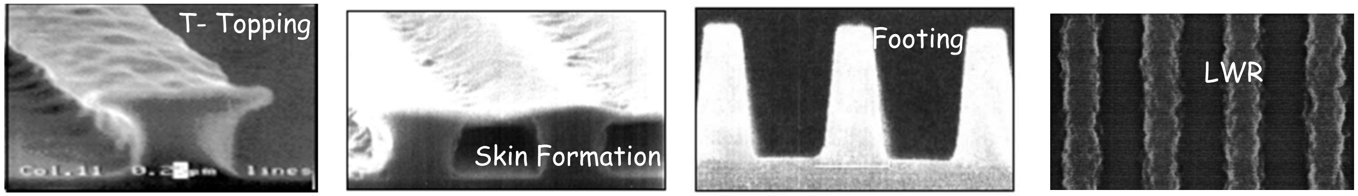
PFOS and other PFCs detected in drinking water resources worldwide

- **PFOS banned for most application is the US and EU.**
- **PFOS listed as chemical for regulation within the Stockholm Convention on Persistent Organic Pollutants (POPs)**
- **EPA Provisional Health Advisory Levels for PFOS 200 ng L^{-1}**

Next Generation PAGs — environmentally friendly

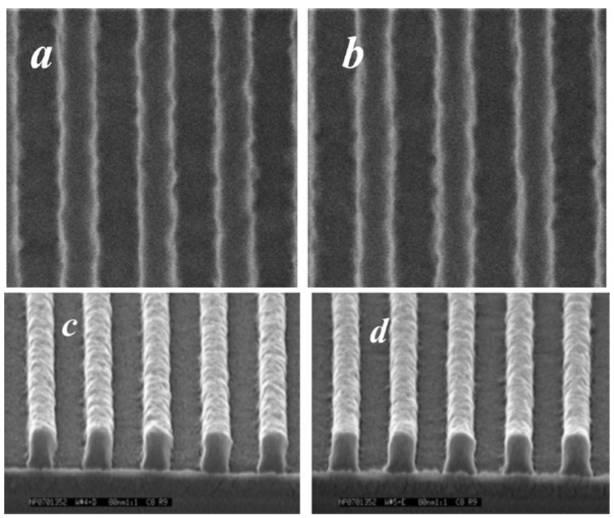
PFOS PAG Performance Issues

“Segregation or non-uniform distribution of PAG”

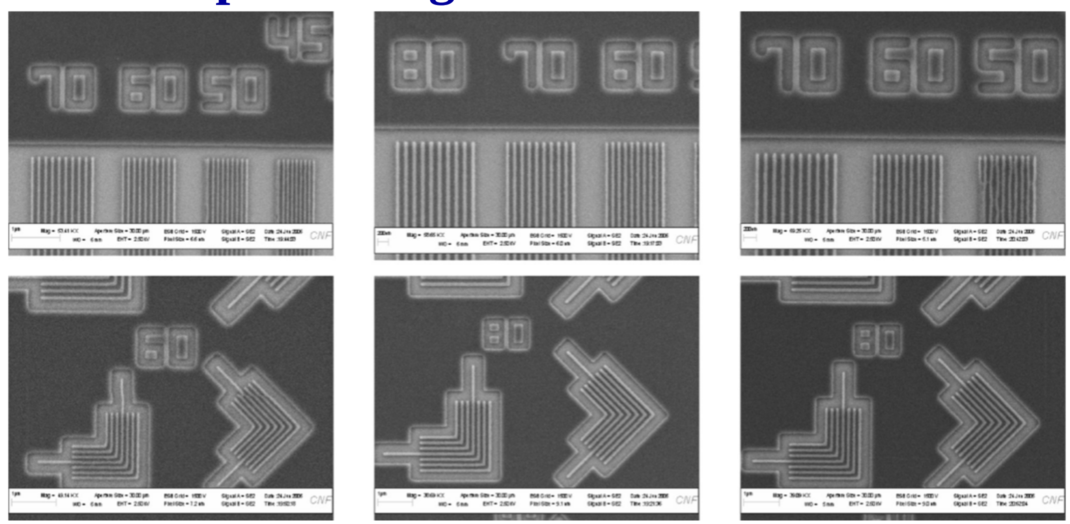


Surface segregation increases with increase in fluorine content

“PFOS free new PAG”: high resolution patterning



Top-down and cross-sectional SEM images of 90 nm dense lines of resist films of TPS NB (a and c) and the sweet PAG (b and d) patterned by 193 nm lithography. Esize (mJ/cm^2): a, 23.8; b, 27.3. LER (nm): a, 5.8; b, 6.5.

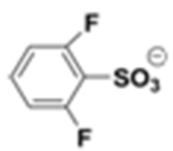


Top-downSEM images of resist films of poly(GBLMA-co-MAdMA) blended separately with TPSGB (left column), TPSNB (middle column), and TPS PFBS (right column) patterned by EUV lithography.

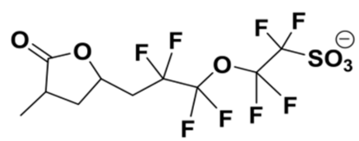
C.K. Ober et al., *Chem. Mater.* (2009); C.K. Ober et al., *JPST* (1999); J. L. Lenhart et al., Langumir (2005); W. Hinsberg et al., SPIE (2004); M. D. Stewart et al., *JVSTB* (2002)

Environmental Compatibility of New Non-PFOS PAG Anions

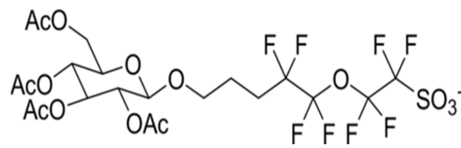
Selected examples:



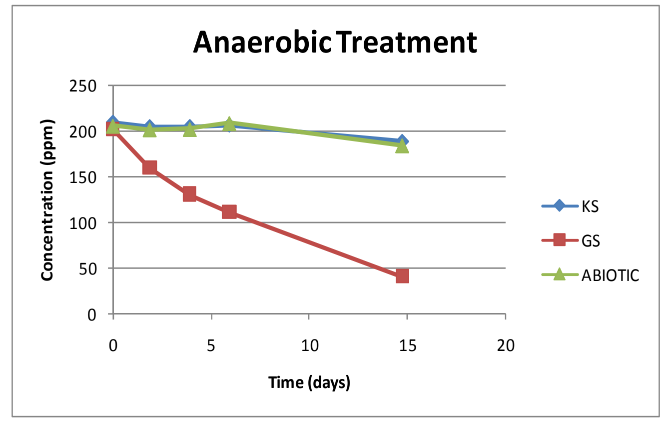
1st generation
(Aromatic structure)



2nd generation
(Aliphatic structure)



3rd generation
(Sugar structure)



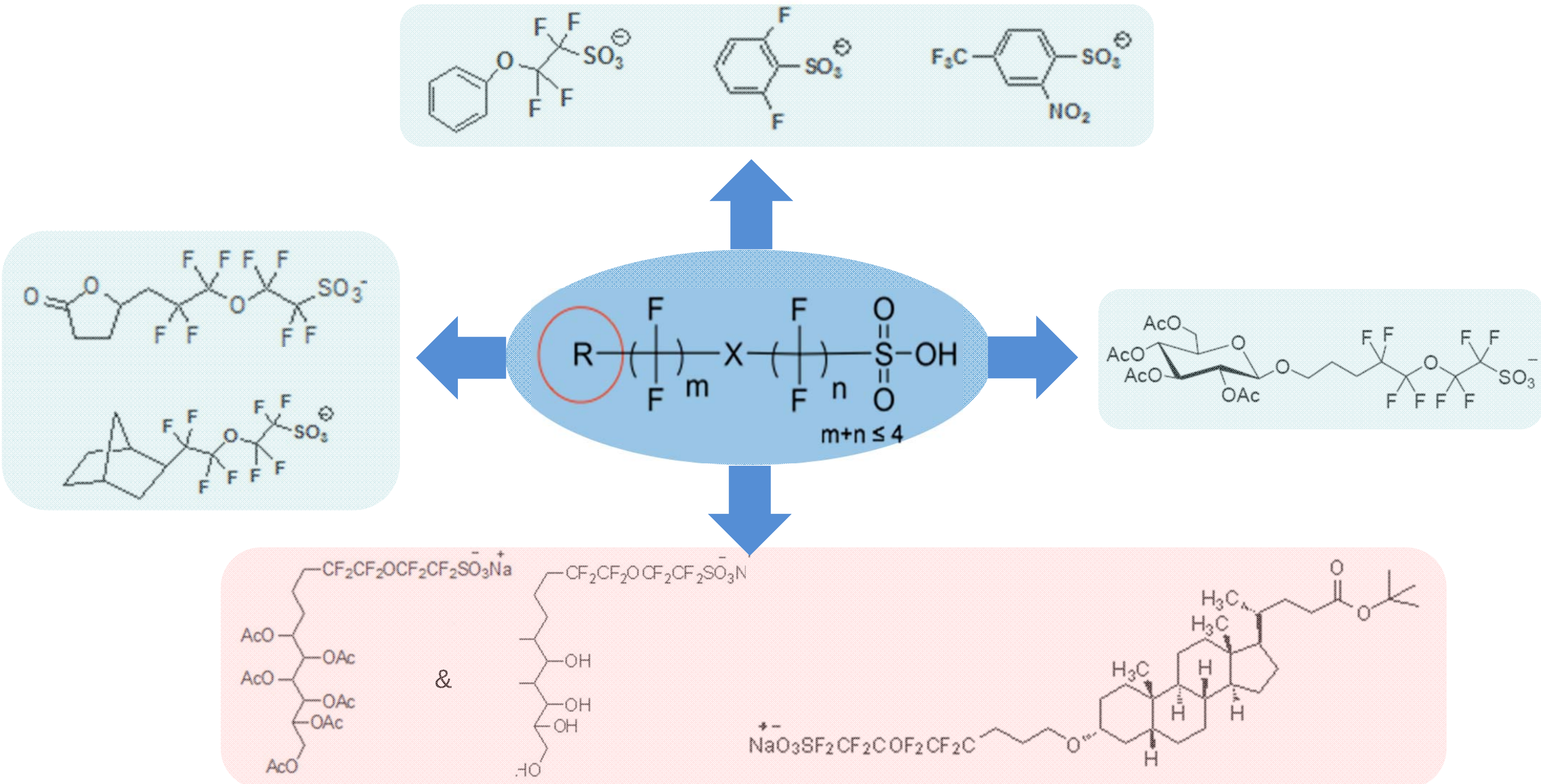
Degradation for 2nd generation PAG in anaerobic batch bioassays. (KS) Abiotic sterilized control; (GS) complete treatment with active sludge; (ABIOTIC) sterile, non-inoculated control.

- **1st Generation Non-PFOS PAGs: Low toxicity and low bioaccumulation potential but relatively persistent to microbial degradation.**
- **2nd Generation Non-PFOS PAGs: Preliminary results show that replacing the phenyl group with a UV-transparent alicyclic moiety increases the susceptibility of the PAG compound to biodegradation.**
- **3rd Generation Non-PFOS PAGs: Replacing with sugar and natural groups is expected to increase biodegradation.**

Molecular Design of New PAGs:

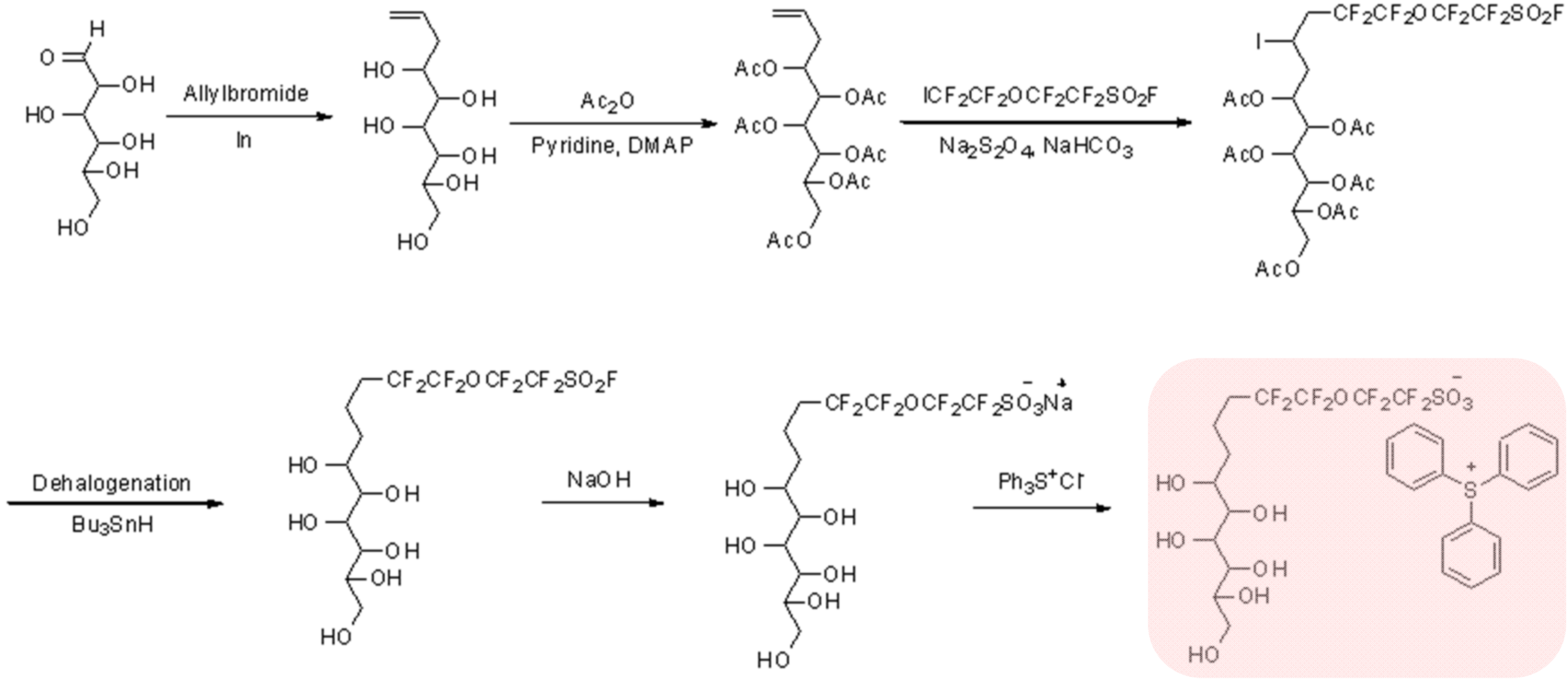
PFOS-free salts

For environmentally friendly and excellent performance:



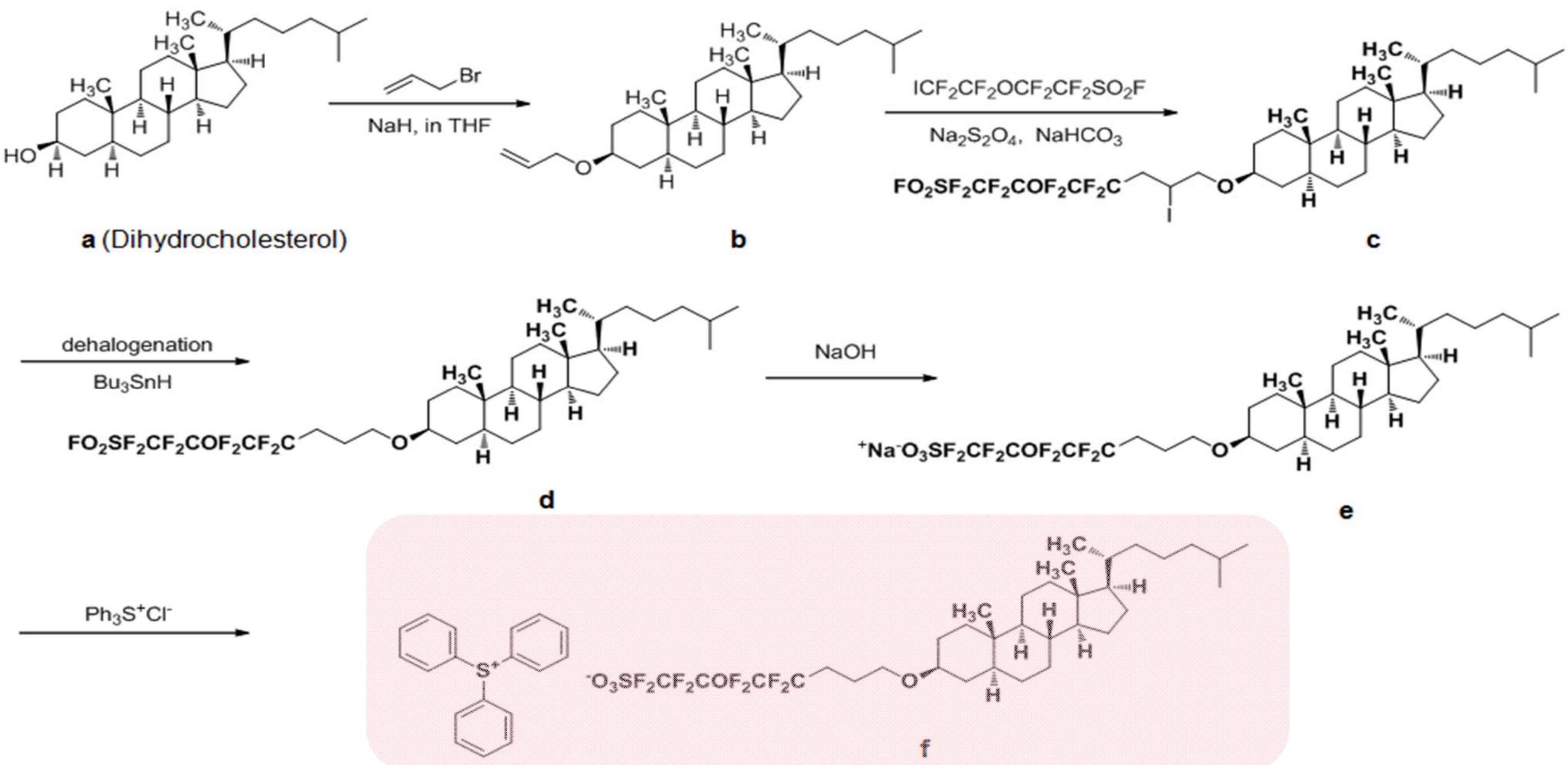
Synthesis of linear type "Sweet" PAG

❖ Synthetic scheme of deacetylated linear type Sweet PAG:



Synthesis of "Biocompatible" PAGs

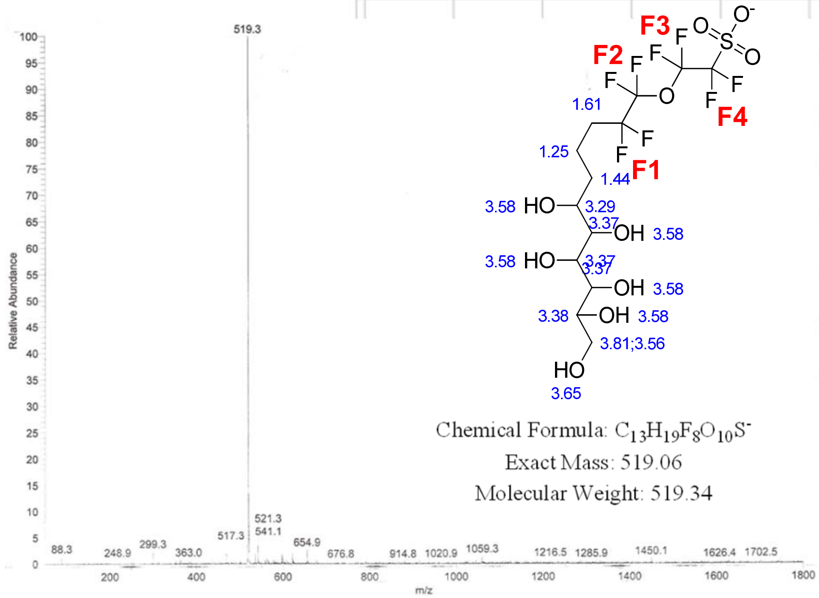
❖ **Synthetic scheme of Dihydrocholesterol based PAG:**

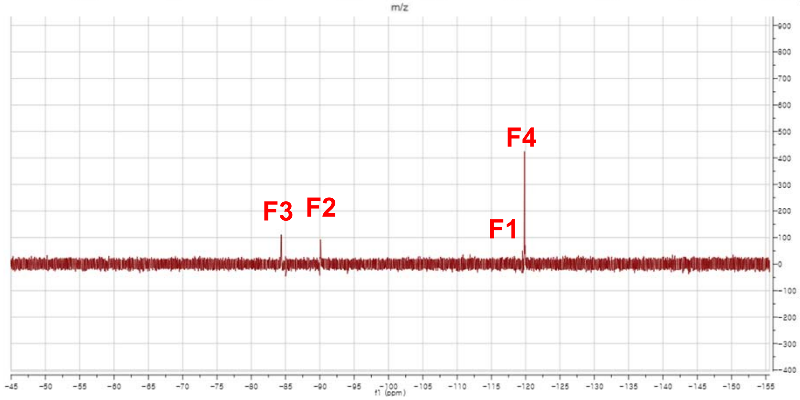


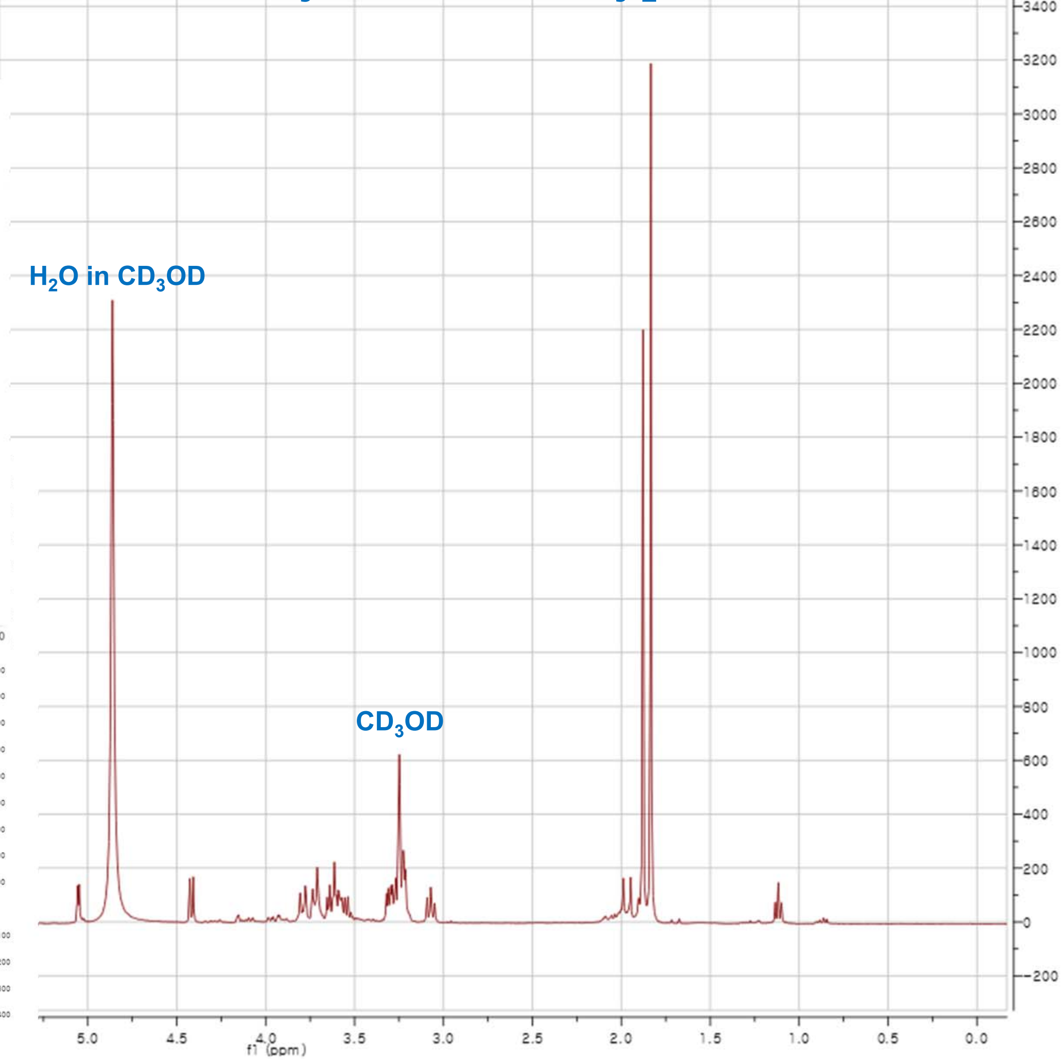
Ongoing..

Characterizations of New PAGs

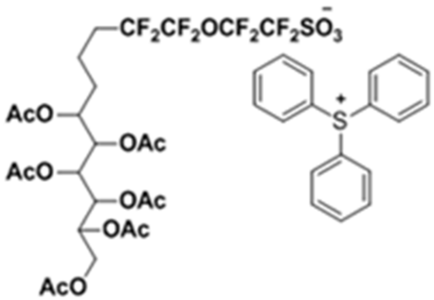
- 1H/19F NMR, Mass Spectra in the deacetylated linear type Sweet PAG



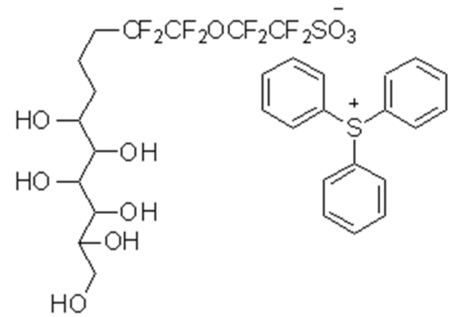




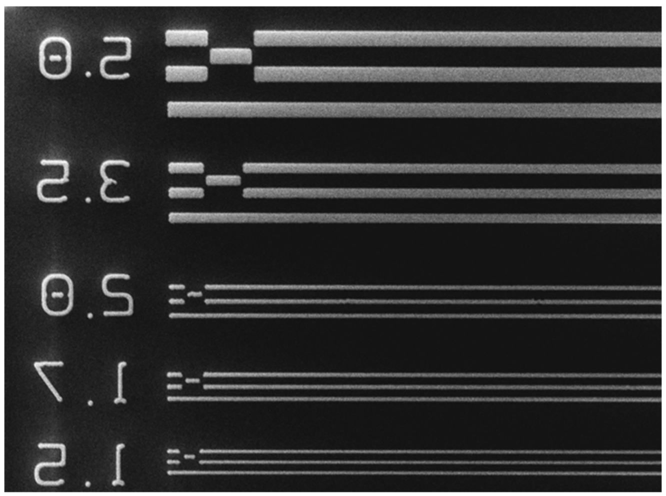
Evaluation of Lithographic Performance

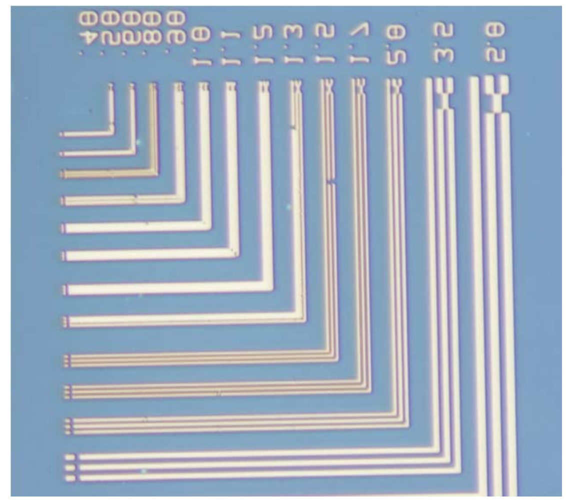


The conditions:
50mg ESCAP
2.5mg PAG (5%)
1.0g PEGMA (5% solution)
PAB: 130℃/60s
PEB: 130℃/60s
Exposure: 20 mJ/cm² at 254nm
Development: 0.26 N TMAH/60s



The conditions:
50mg ESCAP
2.5mg PAG (5%)
1.0g Ethyl lactate (5% solution)
PAB: 130℃/60s
PEB: 130℃/60s
Exposure: 20 mJ/cm² at 254nm
Development: 0.26 N TMAH/60s

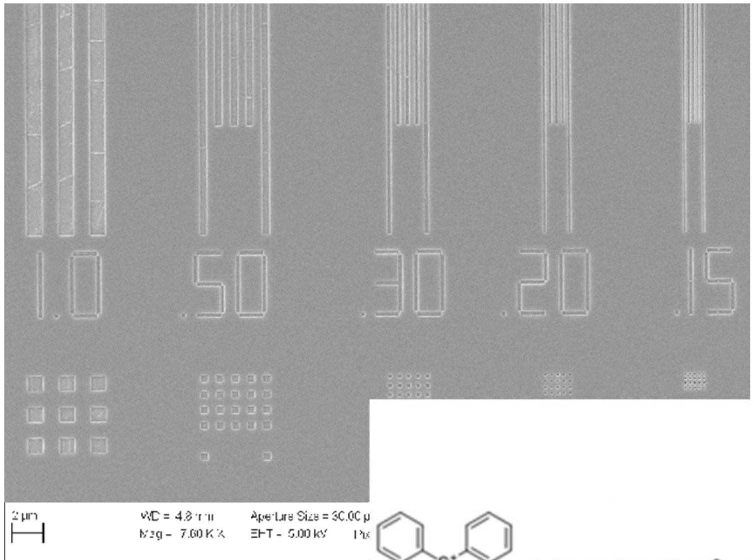


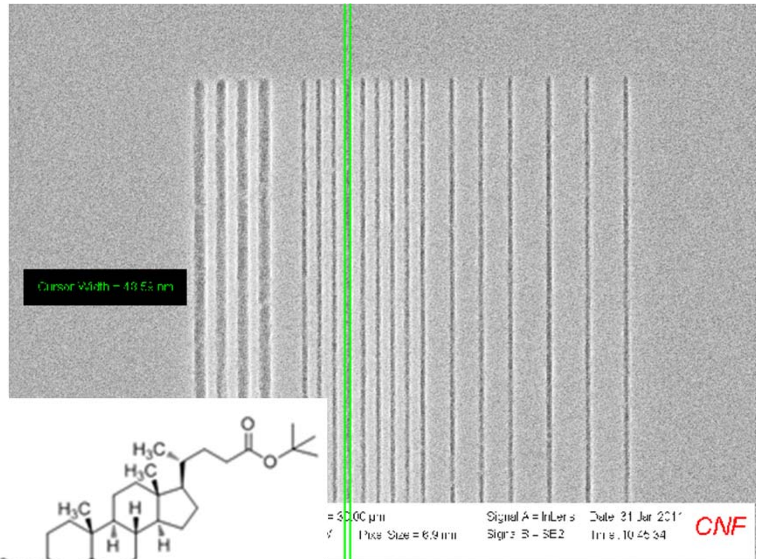


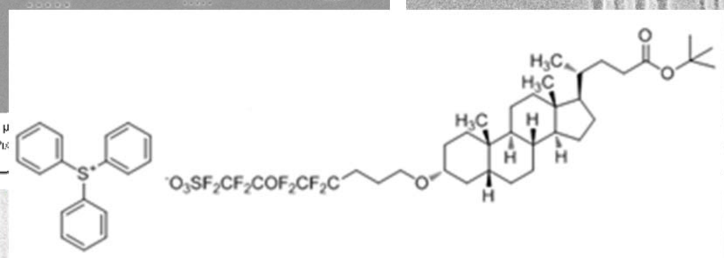
Solvent	PGMEA	Butanone	Ethyl lactate
Solubility of PAG	△	△	O

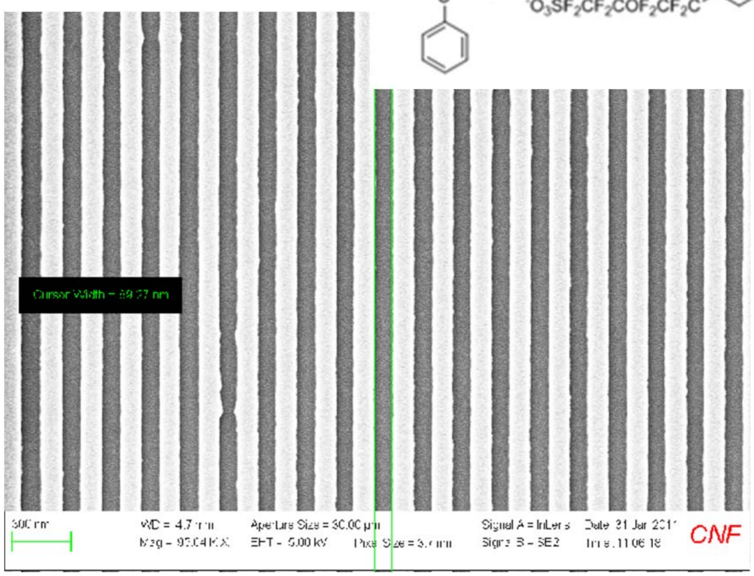
Some issues with solubility of deacetylated linear type Sweet PAG

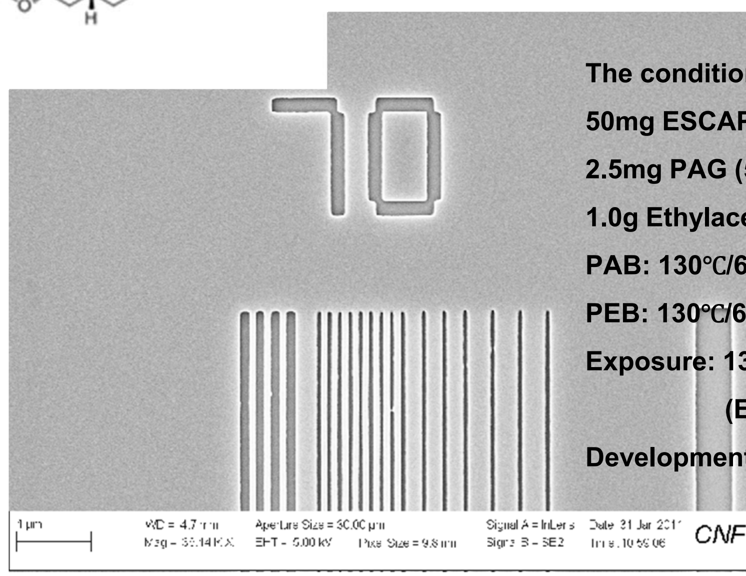
E-beam Lithographic Performance











The conditions:

50mg ESCAP

2.5mg PAG (5%)

1.0g Ethylacetate (5% solution)

PAB: 130℃/60s

PEB: 130℃/60s

Exposure: 130 μc/cm^2 at 100Kev (E-beam)

Development: 0.26 N TMAH/60s

SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Industrial Interactions and Technology Transfer

- **Collaboration with Dow Electronic Materials for photolithography tests of Sweet PAG concluded**
- **Samples provided to Orthogonal, Inc. – a small startup**
- **Performance at 193 nm and EUV evaluated with the assistance of International Sematech**
- **Ongoing interactions with Intel on LER issues**

Future Plans

Next Year's Plans :

- Prepare next generation PAGs (several more compounds) based on biomolecules.
- Evaluate the lithographic performance of new PAGs.
- Modify sulfonium cationic groups.
- Reduce synthetic steps and use more environmentally friendly chemicals.
- Summarize previous studies and submit manuscripts for transfer of know-how to technical community.

Long-Term Plans :

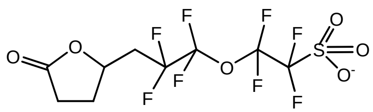
- Establish the relationship between photoacid generators' structure and their environmental properties

Environmental Compatibility of New Non-PFOS PAG Anions

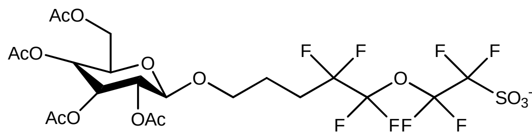
Objectives:

- **Evaluate the environmental compatibility of new PAGs.**
- **Evaluation of selected computer models to predict environmental properties of new PAGs.**

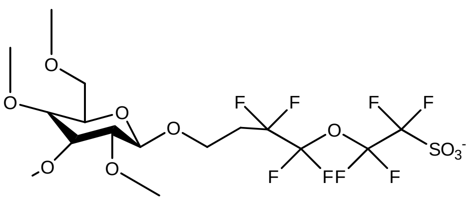
Environmental Compatibility of New Non-PFOS PAG Anions



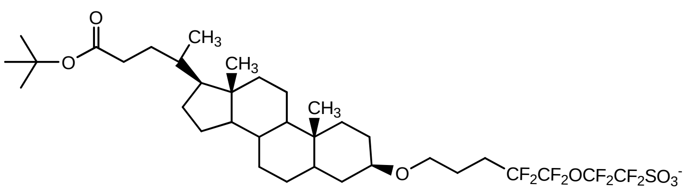
Lactone PAG



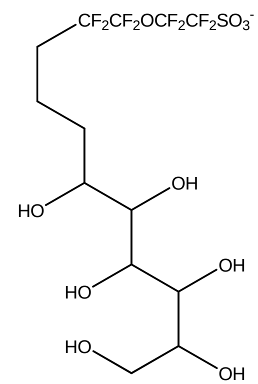
Sugar sweet PAG



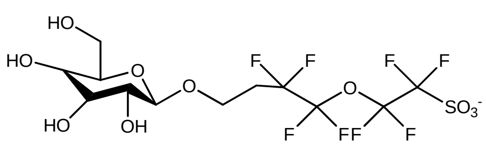
Methoxy sugar B sweet PAG



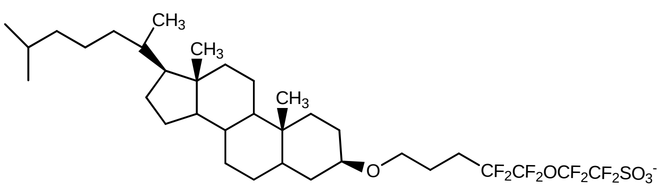
Lithocholic acid PAG



Linear sweet PAG



Hydroxy sugar B sweet PAG



Dihydrocholesterol PAG

- **3rd Generation Non-PFOS PAGs included in the testing program**

Environmental Compatibility

- **Biodegradation**
  - Batch bioassays: aerobic and anaerobic conditions
- **Toxicity**
  - Microbial inhibition (aerobic and anaerobic microorganisms)
  - Aquatic toxicity (Microtox^R with bacterium, *Vibrio fischeri*)
  - MTT test (mitochondrion activity)
  - Real time cell analysis or RTCA (xCELLigence)
- **Bioaccumulation**
  - K_{ow}: water-octanol partition coefficient

Microbial Degradation of New Generation PAGs

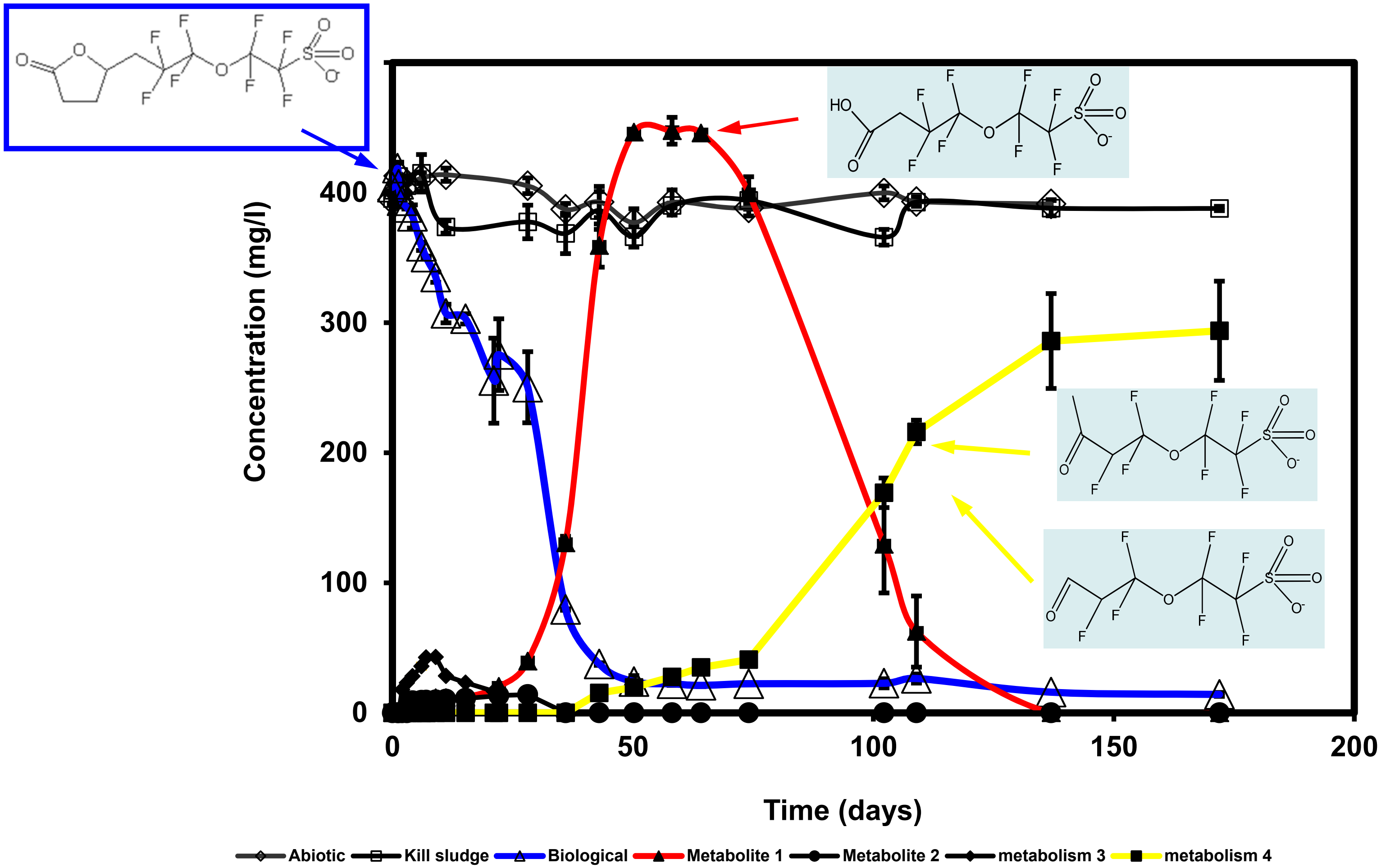
Compounds	Aerobic Degradation	Anaerobic Degradation
PFOS	NO	NO
PFBS	NO	NO
Sweet PAG	YES	YES
Lactone PAG	YES	NO
Linear sweet PAG	YES	NO
Lithocholic acid	In progress	In progress

Biomolecule-based PAGs are degraded by microorganisms in activated sludge.

High PAG removals anticipated in conventional wastewater treatment systems

Microbial Degradation of New Generation PAGs

Biodegradation of the "lactone PAG" by aerobic microorganisms *vs.* time



Biomolecule-based PAGs are readily degradable by aerobic bacteria in activated sludge.

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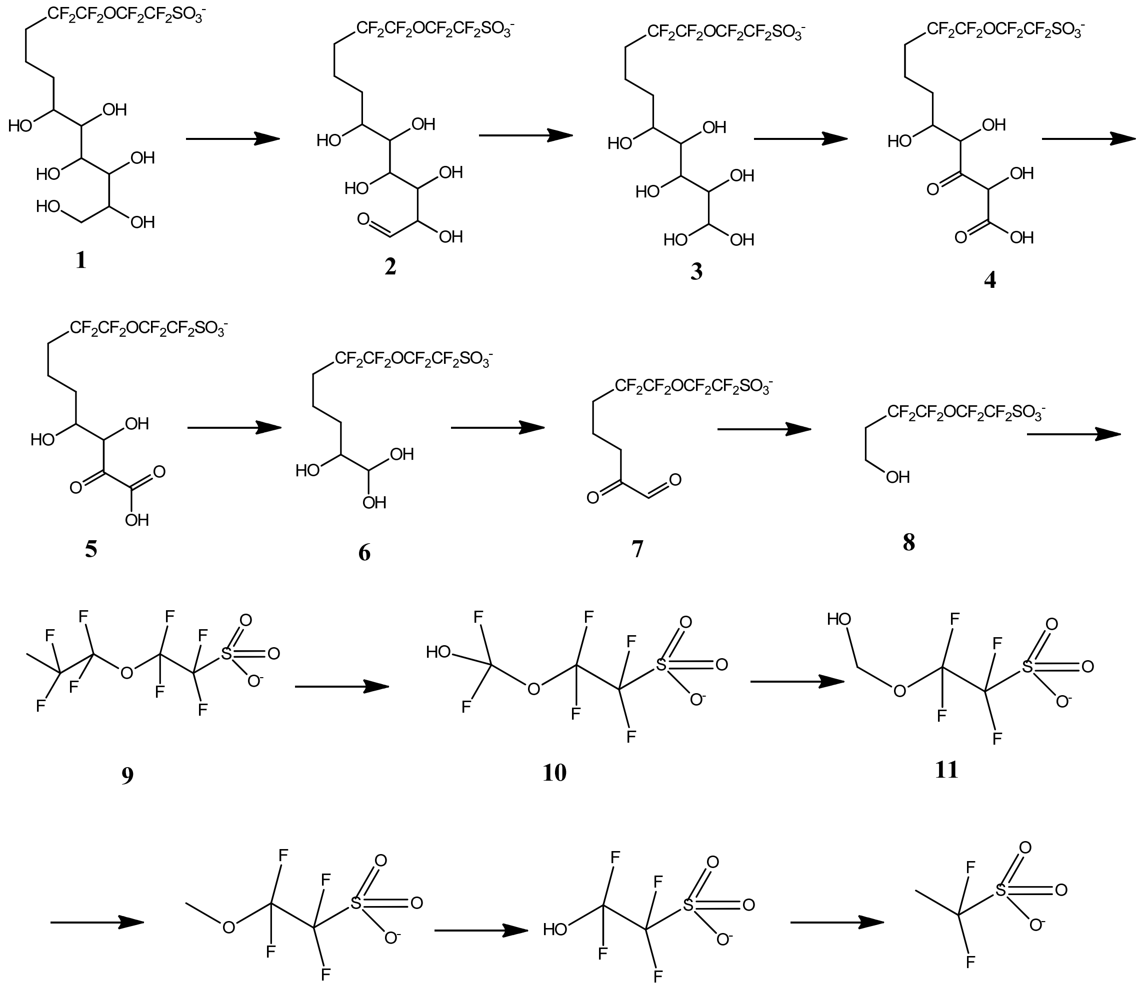
Microbial Degradation of New Generation PAGs

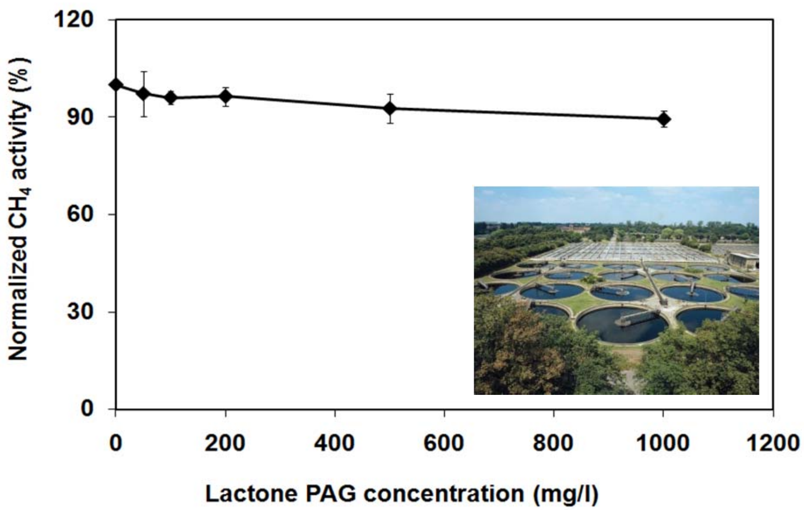
Aerobic biodegradation pathway for the Linear Sweet PAG



Biomolecule-based PAGs are susceptible to aerobic degradation.
Microbial attack of the perfluorinated backbone observed in the assay with linear sweet PAG.

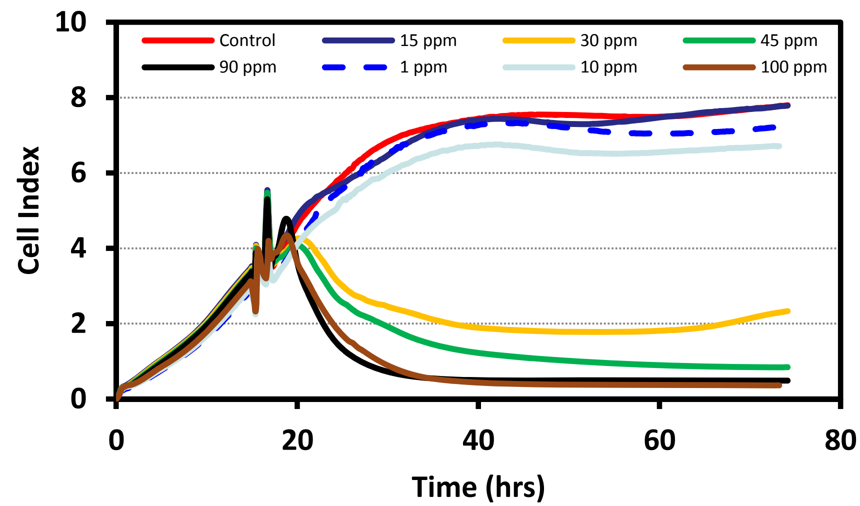
Cytotoxicity of New Generation PAGs

Lactone PAG: Inhibition to methanogens in anaerobic biofilms



PAG compounds are not toxic to anaerobic wastewater treatment biofilms.

Cytotoxicity of sugar Sweet PAG: RTCA with lung epithelial cells



Some PAGs showed intermediate toxicity towards lung epithelial cells (RTCA).

Cytotoxicity of New Generation PAGs

Summary of inhibitory concentrations determined for the PAG compounds in different toxicity assays

Compounds	Microtox		Methanogenic±		RTCA (lung epithelium)	
	IC50¥ (mg/l)	Max Conc. Tested (mg/l)	IC50 (mg/l)	Max Conc. Tested (mg/l)	IC50 (mg/l)	Max Conc. Tested (mg/l)
PFOS	GMC	250	GMC*	250	50.5	63
PFBS	GMC	3,375	GMC	500	85.2	100
Lactone PAG	GMC	1,000	GMC	1,000	GMC	100
Sugar Sweet PAG	3.6	2,500	GMC	500	25.7	100
Linear Sweet PAG	5.6	1,000	GMC	1,000	11.5	100
Lithocholic acid PAG	0.44	200	GMC	100	12.2	100

*GMC= Greater than maximum concentration tested. ¥: Based on the results after exposure time of 30 min.
±: Based on results of two experiments with hydrogen and acetate as electron donor, respectively. $ Testing in progress

- **PAG compounds were not toxic to anaerobic wastewater treatment biofilms.**
- **Some PAG compounds showed high toxicity towards the bacterium *V. fischeri* (Microtox) and intermediate toxicity towards lung epithelial 16HBE14o- cells (RTCA with xCELLigence system)**

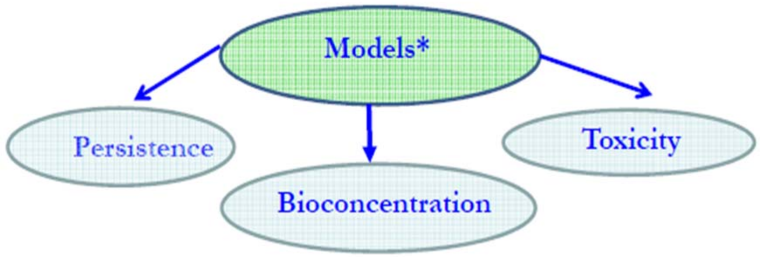
Prediction of Environmental Compatibility using Computer Models

Biodegradation potential and/or pathways

- **EPA Persistence-Bioaccumulation-Toxicity profiler (PBT)[3]**
- **EPA-BIOWIN[4]** (aerobic and anaerobic biodegradation)
- **CATABOL[2]** (degradation of fluorinated compounds)
- **University of Minnesota Biocatalysis/ Biodegradation Database (UMB-BD[1])**

Chemical degradation (Advanced Oxidation)

- **EPA-AOP[4]**



Ecotoxicity

- **PBT profiler** (Chronic fish toxicity)
- **EPA-ECOSAR[4]** (Acute/chronic toxicity to fish, daphnids and green algae)

Bioaccumulation

- **PBT profiler**

[1] ***http://umbbd.msi.umn.edu/index.html,*** **[2]** ***SAK and QSAR in Environ. Res., 2004, 15: 69. [3] http://www.pbtprofiler.net/***
[4] ***http://www.epa.gov/oppt/exposure/pubs/episuite.htm***

Biodegradation Potential: Model Predictions *vs.* Experimental Data

Compounds	Aerobic		Anaerobic	
	Model: BIOWIN	Experimental	Model: BIOWIN	Experimental
PFOS	LOW	LOW	LOW	LOW
PFBS	LOW	LOW	LOW	LOW
Lactone PAG	Intermediate	HIGH	LOW	LOW
Sugar sweet PAG	HIGH	HIGH	LOW	Intermediate
Linear sweet PAG	HIGH	HIGH	LOW	LOW
Lithocholic PAG	LOW	Ongoing	LOW	Ongoing

- **BIOWIN generally provided good predictions of aerobic and anaerobic biodegradation potential**

Prediction of Removal by Advanced Oxidation Processes

Compounds	Removal by Advanced Oxidation Processes (AOPs)	
	AOP Model	Experimental
PFOS	NO	NO
PFBS	NO	NO
Lactone PAG	YES	YES
Sugar sweet PAG	YES	YES
Linear sweet PAG	YES	planned
Lithocholic PAG	YES	planned
Dihydrocholesterol PAG	YES	planned

- **AOP provided good predictions of compound susceptibility to oxidative attack by hydroxyl radicals.**

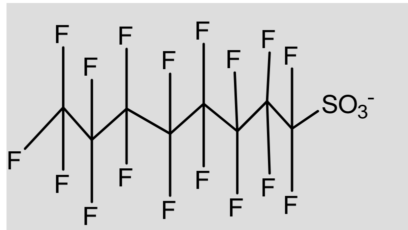
Toxicity: Predicted *vs.* Measured Levels

Compounds	PBT	ECOSAR		Experimental	
	Fish Chronic Tox	Aquatic Chronic Tox	Aquatic Acute Tox	Methanogenic biofilms	Microtox
PFOS	high	intermediate	intermediate	Low	Low
PFBS	low	low	low	Low	Low
Lactone PAG	low	low	low	Low	High
Sugar sweet PAG	low	low	low	Low	High
Linear sweet PAG	low	low	low	low	High
Lithocholic PAG	NE*	High	High	Low	High

* NE = not estimated

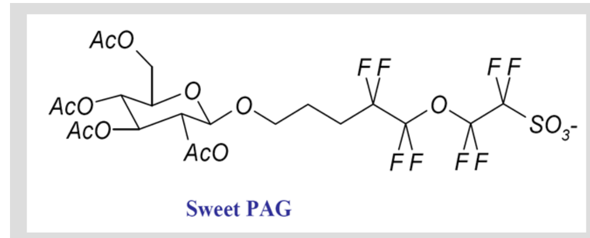
- **PBT and ECOSAR models predicted experimental toxicity data obtained with wastewater microorganisms.**
- **Models showed poor fit with Microtox (bioluminescent bacteria) data.**

Conclusions



PFOS

(Perfluoroalkyl sulfonate)



New generation PAGs

(Biomolecule-based)

Biodegradability	NO	YES (aerobic)
Chemical degradation	NO	YES
Methanogenic toxicity	Low	Low
Cytotoxicity	YES	+ / -- (depends on PAG)
Bioaccumulation	YES	NO

The newly developed, biomolecule-based PAGs present significant ESH advantages compared to PFOS-based PAGs.

Future Plans

Next Year's Plans :

- **Complete environmental evaluation of the new PAGs.**
- **Evaluate the removal of novel PAGs using conventional biological and physico-chemical treatment techniques.**
- **Summarize previous studies and submit manuscripts for transfer of know-how to technical community.**

Long-Term Plans :

- **Establish the relationship between the chemical structure of PAG compounds and their environmental properties.**

Publications, Presentations, and Recognitions/Awards

Publications

- Cho Y., Ouyang C. Y., Sun W., Sierra-Alvarez R., Ober C. K. "Environmentally Friendly Natural Molecules Based Photoacid Generators for the Next Generation Photolithography" *Proc. SPIE*, 2011.
- Yi Y, Ayothi R, Wang Y, Li M, Barclay G, Sierra-Alvarez R, Ober CK. 2009. Sulfonium Salts of Alicyclic Group Functionalized Semifluorinated Alkyl Ether Sulfonates As Photoacid Generators" *Chem. Mater.* 2009, 21, 4037.
- Jing Sha, Byungki Jung, Michael O. Thompson, and Christopher K. Ober. 2009. Submillisecond post-exposure bake of chemically amplified resists by CO2 laser spike annealing. J. Vac. Sci. Technol. B, 27(6), 3020-3024.
- Ayothi R, Yi Y, Cao HB, Wang Y, Putna S, Ober CK. 2007. Arylonium Photoacid Generators Containing Environmentally Compatible Aryloxyperfluoroalkanesulfonate Groups" *Chem. Mater.* 2007, 19, 1434.
- Ober CK, Yi Y, Ayothi R. 2007. Photoacid generator compounds and compositions. *PCT Application* WO2007124092.

Presentations and Conference Proceedings

- Condensed Matter and Materials Physics (CMMP 10). Warwick, UK, Dec. 14-16, 2010. "Will Polymers Be Used to Make the Next Generation Nano World?", invited plenary talk.
- 2010 MRS Fall Meeting, Boston, MA, November 29-December 3, 2010. "Striving for Sub-30 nm Resolution: Directed Assembly Meets Self Assembly", invited talk.
- 1st RX Branch Distinguished Lecture, Air Force Research Laboratory, Dayton, OH, Nov. 1 – 5, 2010. "The convergence of top down and bottom up patterning applied to microelectronics and the life sciences"
- 2010 MRS Spring Meeting, San Francisco, CA, April 5-9, 2010. "Striving for Sub-30 nm Resolution: Using Directed or Self Assembly", invited talk.
- Spring 2010 ACS National Meeting, San Francisco, CA, March 21-25, 2010 "Self-assembly and directed assembly: Tools for current challenges in nanofabrication", invited talk – Lovinger Award Symposium.
- CNF Synergies in NanoScale Manufacturing & Research Workshop, Ithaca, NY, Jan. 29, 2010. "Orthogonal Processing: A New Strategy for Patterning Organic Electronics", invited talk.

Publications, Presentations, and Recognitions/Awards

Presentations and Conference Proceedings

- Sun W, Cho Y,Ober CK, Field JA, Sierra Alvarez R. 2010. Sugar-Based Photoacid Generators ("Sweet" PAGs): Environmentally Friendly Materials for Next Generation Photolithography TECHCON Conference: Technology and Talent for the 21st Century. Austin, TX. Sept. 13-14.
- Sun W, Sierra-Alvarez R, Ober C, Cho Y. 2011. Environmentally Friendly Sugar or Natural Materials Based Photoacid Generators for Next Generation Photolithography. 2nd International Congress on Sustainability Science and Engineering. Jan. 9-14, Tucson, AZ.

Recognitions/Awards

- 2009 Gutenberg Research Awards for C. K. Ober
- 2009 Fellow of the American Chemical Society for C. K. Ober

Task Deliverables

- Report on the preparation of new "Sweet" PAG Gen 2 materials (Jan 10)
  - *completed*

- Report on the lithographic evaluation of new "Sweet" PAG Gen 2 materials (July 10)
  - *completed*

- Report on the assessment of the environmental compatibility of 2nd generation "Sweet" PAGs (Jan 11)
  - *completed*

- Report on the evaluation of selected computer models to predict PAG environmental fate (Jan 11)
  - *completed*

- Report on the preparation of new "Sweet" PAG Gen 3 materials (Jan 11)
  - *completed*

Students on Task 425.029

- **Graduated Students and Current Affiliation**
  - Nelson Felix, IBM, Dec 2007
  - Victor Gamez, CH2M Hill, May 2009
  - Evan Schwartz, 3M
  - Jing Sha, Intel
- **Internships (Task and related students)**
  - Marie Krysak, Intel
  - Evan Schwartz, Intel & Bayreuth
  - Anuja de Silva, IBM (now at IBM)
  - Jing Sha, NIST

Prediction of Toxicity and Environmental Fate using Computer Models

- **Strategies to increase (bio)degradability: Biodegradation testing of structurally-related compounds modified with selected functionalities.**
- **Testing the validity of selected models to predict the toxicity, (bio)degradation potential and other properties determining the environmental fate of PAGs.**